

PATENT ABSTRACTS OF JAPAN

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(54) NONAQUEOUS SECONDARY BATTERY

(57)Abstract:

PURPOSE: To provide a nonaqueous secondary battery with large capacity, having a positive electrode, a negative electrode, and an electrolyte prepared by dissolving an electrolyte in a nonaqueous solvent by using a carbonaceous material crushed with a jet mill as a negative electrode material.

CONSTITUTION: A nonaqueous secondary battery is obtained by interposing a separator impregnated with an electrolyte prepared by dissolving an electrolyte such as LiBF₄ in a nonaqueous solvent such as propylene carbonate between a positive electrode comprising LiCoO₂ and a negative electrode comprising a carbonaceous material. As the carbonaceous material of the negative electrode material, the material crushed with a jet mill is used. The material obtained by crushing coke so as to have a particle size of around 60 μ m with the jet mill with an air speed of 10m/sec or more is preferable. The negative electrode is prepared by baking the coke powder at 1100°C or so, mixing with a binder such as PP, and press-molding.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to a nonaqueous secondary battery. It is related more detailed especially with nonaqueous secondary batteries suitable as a small and lightweight object for electronic equipment including a lithium secondary battery.

[0002]

[Description of the Prior Art]In recent years, from the position of small weight savings, such as electronic equipment, power-saving, and environmental protection, the clean nonaqueous cell replaced with a lead storage battery or a nickel cadmium cell, especially the lithium secondary battery attracted attention, and even the utilization stage was reached. However, when the lithium metal was used for the negative electrode, the lithium metal grew in the shape of a dendrite at the time of charge, and there was a problem of causing an internal short circuit. As the measure, development of the material which can absorb and emit a lithium metal atom is performed briskly, and promising ** of what used corks also in it is carried out in respect of low cost and high capacity (JP,62-90863,A, JP,1-221859,A, JP,63-121257,A).

[0003]

[Problem(s) to be Solved by the Invention]However, although many proposals about the cell of a high characteristic are made, the actual condition is that the corks of a Carboniferous system or a petroleum system are excellent practical. If it is mentioned that the ratio of the charge-and-discharge capacity of the 2nd henceforth to the 1st charging capacity is low as a difficulty of these corks and this ratio is low, many positive electrode materials are needed and it is not desirable. That is, the actual condition is having to stuff into a cell the positive electrode material which is not kept in capacity, and a capacity rise having a limit as a cell, and becoming a cell in an anode, and becoming high also in cost. Rather, when this capacity factor considers a system called a cell, it has a merit dramatically rather than raising capacity, with

this capacity factor maintained.

[0004]

[Means for Solving the Problem]this invention person reached this invention, as a result of examining many things, in order to solve the above-mentioned technical problem. That is, in a nonaqueous secondary battery provided with an electrolysis solution in which an electrolyte was dissolved into an anode, a negative electrode, and a nonaqueous solvent, a gist of this invention is in a nonaqueous secondary battery using as a negative pole material a carbonaceous material by which jet mill grinding was carried out.

[0005]Hereafter, this invention is explained in detail. In this invention, with a carbonaceous material, an FCC (fluidized catalytic cracking) residue oil, Carboniferous system heavy oil, such as petroleum system heavy oil, such as an ordinary pressure residue oil and a decompression residue oil, and a coal tar pitch, a delayed coker, It caulks with autoclave etc., raw coke is obtained, and a thing which made 900-1500 °C calcinate this with a rotary kiln, an electric furnace, etc., and a thing which made 900-1500 °C calcinate phenol resin, furan resin, polyimide resin, etc. further are raised. a ratio of charge-and-discharge capacity of the 2nd henceforth to the 1st charging capacity in the superfines end of carbide of a resin system is quite low -- moreover -- this -- since the ratio is low in value, an effect of this invention is relatively large in a carbonaceous material of resin system origin.

[0006]In this invention, a jet mill grinds these carbonaceous materials (it may be before the above-mentioned calcination). Using wind force energy, this jet mill aims at a particle comrade's collision, is a grinder which performs pulverizing effectively and is ground with impact velocity of 1 m/sec or more. And especially in this invention, it is preferred from the moldability of a battery electrode sheet, and a point of electrode bulk density to grind at not less than 10 m/sec high impact speed.

[0007]It is not needlelike and grinding shape is considered because [as / at low impact velocity] becomes a block-like-shape fragment easily by grinding at such a high impact speed. According to jet mill grinding of this invention, the superfines end of about 1 micrometer or less adhering to the surface of carbonaceous material particles is reduced or removed remarkably. Thereby, it is surmised that a ratio of the aforementioned charge-and-discharge capacity will improve.

[0008]In this invention, the end of superfines which jet mill grinding of the carbonaceous material ground with grinders other than a jet mill was carried out (with for example, less than 10 m/sec low impact velocity), and adhered to the surface is also removable. With a jet mill, 60 micrometers or less of particle diameter of a carbonaceous material are suitably ground by about 50 micrometers or less still more preferably.

[0009]This carbonaceous material can be used as a negative electrode material of a nonaqueous secondary battery with a conventional method. Conventionally, it may be used for

a nonaqueous secondary battery and is not limited in particular for an electrolysis solution to which it makes it come to dissolve an electrolyte into an anode and a nonaqueous solvent. Specifically as an anode, LiCoO_2 , MnO_2 , TiS_2 , FeS_2 , Nb_3S_4 , Mo_3S_4 , CoS_2 , and V_2O_5 , P_2O_5 , CrO_3 , V_3O_8 , TeO_2 , GeO_2 , etc. as an electrolyte, LiClO_4 , LiBF_4 , LiPF_6 , etc. as a nonaqueous solvent which dissolves an electrolyte, Propylene carbonate, a tetrahydrofuran, 1,2-dimethoxyethane, dimethyl sulfoxide, dioxolane, dimethylformamide, dimethylacetamides, two or more sorts of these mixed solvents, etc. are used.

[0010]Especially, the most desirable combination is LiCoO_2 - LiPF_6 -propylene carbonate and 1 and 2-dimethoxyethane. In order to make internal resistance of a cell small, a porous body is preferred for a separator, and a thing of organic solvent-proof nature materials, such as nonwoven fabrics, such as polypropylene, and a glass filter, is used.

[0011]As for these negative electrodes, an anode, an electrolysis solution, and a separator, it is common to include in a cell case which carried out the nickel plate, for example to a stainless steel or this. A method of inserting an anode of a pellet type and a disc-like negative electrode in spiral structure or a button type case which made a band-like anode and a negative electrode spiral via a separator as battery structure via a separator, etc. are adopted.

[0012]

[Example]Hereafter, although an example explains this invention still in detail, this invention is not limited to these examples, unless the gist is exceeded.

[0013]Example 1 coal tar pitch was heat-treated with autoclave for 480 ** and 30 hours, and raw coke was obtained. The jet mill (10 m/(sec)) ground this raw coke to 44 micrometers or less, it calcinated at 1100 ** succeedingly for 3 hours, and the corks of this invention were obtained.

[0014]Pressing of what was mixed with the corks and polypropylene powder which were obtained by the weight ratio of 90:10 was carried out, and it was created. The counter electrode and the reference pole created 3 pole type glass cell using Li. What dissolved LiPF_6 in propylene carbonate (PC) at a rate of 1 mol/l. as an electrolyte was used for the electrolysis solution. About the capacity of this cell, compared with an anode, the negative electrode was made small enough and it has set up become negative-electrode rule. Making this cell into charging current and discharge current 1 mA/cm^2 , 0.01V and the discharge of charge went to 1.0V. As a result, the ratio of the 2nd henceforth to the 1st charge was 78%.

[0015]The half section figure of the button type nonaqueous secondary battery as an example of this invention is shown in drawing 1. Here, the negative electrode 1 comprises corks of this invention. This negative electrode is joined to the inner surface of the negative pole collector 2. This charge collector 2 has adhered to the inside of the negative electrode can 3 which consists of ferritic stainless steel (SUS430).

[0016]The peripheral edge of said negative electrode can 3 is being fixed to the inside of the insulating packing 4 made from polypropylene.

The positive electrode can 5 is being fixed to the counter direction in said negative electrode can 3 which becomes a periphery of the insulating packing 4 from stainless steel.

The positive pole collector 6 is being fixed to the inner bottom of this positive electrode can 5, and the anode 7 is being fixed to the inner surface of this positive pole collector 6. The separator intervenes between this anode 7 and said negative electrode 1.

The electrolysis solution in which the electrolyte was dissolved is impregnated here.

[0017]And said negative electrode carried out pressing of what was mixed with this invention corks and polypropylene powder by the weight ratio of 90:10, and created it. The anode carried out pressing of what mixed LiCoO_2 , acetylene black as a conducting agent, and the fluoro-resin as a binder by the weight ratio of 85:10:5, and created it. What dissolved LiPF_6 in propylene carbonate (PC) at a rate of 1 mol/l. as an electrolyte was used for the electrolysis solution. About the capacity of this cell, compared with an anode, the negative electrode was made small enough and it has set up become negative-electrode rule. Making this cell into charging current and discharge current 1 mA/cm^2 , charge went to 3.6V and discharge went to 2.5V. The cell capacity was 12.5mAh.

[0018]Corks were obtained like Example 1 except having used the hammermill instead of the jet mill of comparative example 1 Example 1. As a result, the ratio of the 2nd henceforth to the 1st charge was 70%. The cell capacity was 11.1mAh.

[0019]Jet mill grinding of the phenol resin carbonized in 21000 ** of the examples was carried out like Example 1, and the target carbonaceous material was obtained. As a result, the ratio of the 2nd henceforth to the 1st charge was 70%. The cell capacity was 10.0mAh.

[0020]It was made to be the same as that of Example 2 except having used the hammermill instead of the jet mill of comparative example 2 Example 2. As a result, the ratio of the 2nd henceforth to the 1st charge was 60%. The cell capacity was 8.6mAh.

[0021]

[Effect of the Invention]Let the carbonaceous material ground with the jet mill be a negative electrode material in this invention.

Therefore, a nonaqueous secondary battery with big ** and service capacity is provided.

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CLAIMS

[Claim(s)]

[Claim 1]A nonaqueous secondary battery using as a negative pole material a carbonaceous material by which jet mill grinding was carried out in a nonaqueous secondary battery provided with an electrolysis solution in which an electrolyte was dissolved into an anode, a negative electrode, and a nonaqueous solvent.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a section explanatory view of the button type nonaqueous electrolyte secondary battery which is an example of this invention nonaqueous secondary battery.

[Description of Notations]

- 1 Negative electrode,
- 2 Negative pole collector,
- 3 Negative electrode can,
- 4 Insulating packing,
- 5 Positive electrode can,
- 6 Positive pole collector,
- 7 Anode.

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DRAWINGS

[Drawing 1]

